

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
18 September 2003 (18.09.2003)

PCT

(10) International Publication Number
WO 03/076690 A1

(51) International Patent Classification⁷: C25C 3/28

(21) International Application Number: PCT/AU03/00306

(22) International Filing Date: 13 March 2003 (13.03.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PS 1071 13 March 2002 (13.03.2002) AU
PS 3049 19 June 2002 (19.06.2002) AU

(71) Applicant (for all designated States except US): BHP BILLITON INNOVATION PTY LTD [AU/AU]; 600 Bourke Street, Melbourne, Victoria 3000 (AU).

(72) Inventors; and

(75) Inventors/Applicants (for US only): STREZOV, Les [AU/AU]; 7 Marin Street, Adamstown, New South Wales

2289 (AU). RATCHEV, Ivan [AU/AU]; 2 Young Street, Georgetown, New South Wales 2298 (AU). OSBORN, Steve [AU/AU]; 15 Robertson Road, Valentine, New South Wales 2280 (AU).

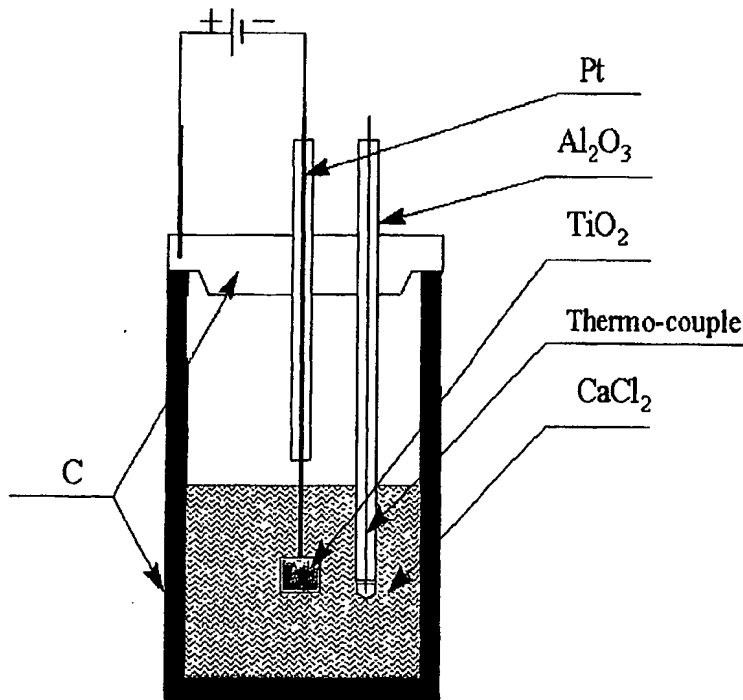
(74) Agent: GRIFFITH HACK; 509 St Kilda Road, Melbourne, Victoria 3004 (AU).

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),

[Continued on next page]

(54) Title: REDUCTION OF METAL OXIDES IN AN ELECTROLYTIC CELL



Schematic of the experimental set up

(57) Abstract: A method of reducing a metal oxide, such as titania in a solid state in an electrolytic cell is disclosed. The electrolytic cell includes an anode, a cathode, and a molten electrolyte. The electrolyte includes cations of a metal that is capable of chemically reducing the metal oxide. The metal oxide in a solid state is immersed in the electrolyte. The method includes a step of operating the cell at a potential that is above a potential at which cations of the metal that is capable of chemically reducing the metal oxide deposit as the metal on the cathode, whereby the metal chemically reduces the metal oxide.

WO 03/076690 A1

Best Available Copy

WO 03/076690 A1



European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— with international search report

- 1 -

REDUCTION OF METAL OXIDES IN AN ELECTROLYTIC CELL

The present invention relates to reduction of metal oxides in a solid state in an electrolytic cell.

5

The present invention was made during the course of an on-going research project on solid state reduction of titania (TiO_2) carried out by the applicant.

10

During the course of the research project the applicant carried out experimental work on the reduction of titania using an electrolytic cell that included a graphite crucible that formed an anode of the cell, a pool of molten CaCl_2 -based electrolyte in the crucible, and a range of cathodes that included solid titania.

15

One objective of the experimental work was to reproduce the results reported in International application PCT/GB99/01781 (publication no. WO99/64638) in the name of Cambridge University Technical Services Limited and in technical papers published by the inventors of that International application.

20

The Cambridge International application discloses two potential applications of a "discovery" in the field of metallurgical electrochemistry.

25

One application is the direct production of a metal from a metal oxide.

30

In the context of this application, the "discovery" is the realisation that an electrolytic cell can be used to ionise oxygen contained in a metal oxide so that the oxygen dissolves in an electrolyte. The Cambridge International application discloses that when a suitable potential is applied to an electrolytic cell with a metal oxide as a cathode, a reaction occurs whereby

35

- 2 -

oxygen is ionised and is subsequently able to dissolve in the electrolyte of the cell.

European patent application 9995507.1 derived
5 from the Cambridge International application has been allowed by the European Patent Office.

The allowed claims of the European patent application *inter alia* define a method of electrolytically
10 reducing a metal oxide (such as titania) that includes operating an electrolytic cell at a potential at an electrode formed from the metal oxide that is lower than the deposition potential of cations in the electrolyte at a surface of the electrode.

15

The Cambridge European patent application does not define what is meant by deposition potential and does not include any specific examples that provide values of the deposition potential for particular cations.

20

However, submissions dated 2 October 2001 to the European Patent Office by the Cambridge patent attorneys, which pre-dated the lodgement of the claims that were ultimately allowed, indicate that they believe that the
25 decomposition potential of an electrolyte is the deposition potential of a cation in the electrolyte.

Specifically, page 5 of the submissions state
that:

30

*"The second advantage described above is achieved in part through carrying out the claimed invention below the decomposition potential of the electrolyte. If higher potentials are used then, as noted in D1 and D2, the
35 cation in the electrolyte deposits on the metal or semi-metal compound. In the example of D1, this leads to calcium deposition and therefore consumption of this*

- 3 -

reactive metal.....During operation of the method, the electrolytic cation is not deposited on the cathode".

Contrary to the findings of Cambridge, the experimental work carried out by the applicant has established that it is essential that the electrolytic cell be operated at a potential that is above the potential at which Ca^{++} cations in the electrolyte can deposit as Ca metal on the cathode.

Accordingly, the present invention provides a method of reducing a metal oxide in a solid state in an electrolytic cell, which electrolytic cell includes an anode, a cathode, a molten electrolyte, the electrolyte includes cations of a metal that is capable of chemically reducing the metal oxide, and the metal oxide in a solid state immersed in the electrolyte, and which method includes a step of operating the cell at a potential that is above a potential at which cations of the metal that is capable of chemically reducing the metal oxide can deposit as the metal on the cathode, whereby the metal chemically reduces the metal oxide.

The applicant does not have a clear understanding of the electrolytic cell mechanism at this stage.

Nevertheless, whilst not wishing to be bound by the comments in this and the following paragraphs, the applicant offers the following comments by way of an outline of a possible cell mechanism.

The experimental work carried out by the applicant produced evidence of Ca metal dissolved in the electrolyte. The applicant believes that, at least during the early stages of operation of the cell, the Ca metal was the result of electrodeposition of Ca^{++} cations as Ca metal on electrically conductive sections of the cathode.

- 4 -

The experimental work was carried out using a CaCl_2 -based electrolyte at a cell potential below the decomposition potential of CaCl_2 . The applicant believes that the initial deposition of Ca metal on the cathode was due to the presence of Ca^{++} cations and O^{--} anions derived from CaO in the electrolyte. The decomposition potential of CaO is less than the decomposition potential of CaCl_2 . In this cell mechanism the cell operation is dependent, at least during the early stages of cell operation, on decomposition of CaO, with Ca^{++} cations migrating to the cathode and depositing as Ca metal and O^{--} anions migrating to the anode and forming CO and/or CO_2 (in a situation in which the anode is a graphite anode).

The applicant believes that the Ca metal that deposited on electrically conductive sections of the cathode was deposited predominantly as a separate phase in the early stages of cell operation and thereafter dissolved in the electrolyte and migrated to the vicinity of the titania in the cathode and participated in chemical reduction of titania.

The applicant also believes that at later stages of the cell operation part of the Ca metal that deposited on the cathode was deposited directly on partially deoxidised titanium and thereafter participated in chemical reduction of titanium.

The applicant also believes that the O^{--} anions, once extracted from the titania, migrated to the anode and reacted with anode carbon and produced CO and/or CO_2 (and in some instances CaO) and released electrons that facilitated electrolytic deposition of Ca metal on the cathode.

Preferably the cathode is formed at least in part

- 5 -

from the metal oxide.

Preferably the method includes operating the cell at the potential that is above the potential at which cations of the metal that is capable of chemically reducing the metal oxide deposit as the metal on the cathode so that the metal deposits on the cathode.

Preferably the metal deposited on the cathode is soluble in the electrolyte and can dissolve in the electrolyte and thereby migrate to the vicinity of the metal oxide.

In a situation in which the metal oxide is a titanium oxide, such as titania, it is preferred that the electrolyte be a CaCl_2 -based electrolyte that includes CaO as one of the constituents of the electrolyte. In this context, it is noted that the present invention does not require the addition of substantial amounts of CaO to the electrolyte.

In such a situation it is preferred that the cell potential be above a potential at which Ca metal can deposit on the cathode, i.e. at a potential that is above the decomposition potential of CaO .

The decomposition potential of CaO can vary over a considerable range depending on factors such as the composition of the anode, the electrolyte temperature and electrolyte composition.

In a cell containing CaO saturated CaCl_2 at 1373K (1100°C) and a graphite anode this would require a minimum cell potential of 1.34V.

It is also preferred that the cell potential be below the potential at which Cl^- anions can deposit on the

- 6 -

anode and form chlorine gas, i.e. the decomposition potential of CaCl_2 .

5 In a cell containing CaO saturated CaCl_2 at 1373K (1100°C) and a graphite anode this would require that the cell potential be less than 3.5V.

10 The decomposition potential of CaCl_2 can vary over a considerable range depending on factors such as the composition of the anode, the electrolyte temperature and electrolyte composition.

15 For example, a salt containing 80% CaCl_2 and 20% KCl at a temperature of 900K (657°C), decomposes to Ca (metal) and Cl_2 (gas) above 3.4V and a salt containing 100% CaCl_2 at 1373K (1100°C) decomposes at 3.0V.

20 In general terms, in a cell containing CaO-CaCl_2 salt (not saturated) at a temperature in the range of 600-1100°C and a graphite anode it is preferred that the cell potential be between 1.3 and 3.5V.

25 The CaCl_2 -based electrolyte may be a commercially available source of CaCl_2 , such as calcium chloride dihydrate, that partially decomposes on heating and produces CaO or otherwise includes CaO .

30 Alternatively, or in addition, the CaCl_2 -based electrolyte may include CaCl_2 and CaO that are added separately or pre-mixed to form the electrolyte.

It is preferred that the anode be graphite or an inert anode.

35 The applicant found in the experimental work that there were relatively significant amounts of carbon transferred from the graphite anode to the electrolyte and

- 7 -

to a lesser extent, to the titanium produced at the cathode under a wide range of cell operating conditions.

Carbon in the titanium is an undesirable
5 contaminant. In addition, carbon transfer was partially responsible for low energy efficiency of the cell. Both problems could present significant barriers to commercialisation of electrolytic reduction technology.

10 The applicant also found that the dominant mechanism of carbon transfer is electrochemical rather than erosion and that one way of minimising carbon transfer and therefore contamination of titanium produced
15 at the cathode by electrochemical reduction of titania is to position a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms between the cathode and the anode and thereby prevent migration of carbon to the cathode.

20 Accordingly, in order to minimise contamination of titanium produced at the cathode resulting from carbon transfer, it is preferred that the electrolytic cell includes a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms
25 positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode.

The membrane may be formed from any suitable material.

30

Preferably the membrane is formed from a solid electrolyte.

One solid electrolyte tested by the applicant is
35 yttria stabilised zirconia.

According to the present invention there is also

- 8 -

provided an electrolytic cell as described above and operating in accordance with the above described method.

5 The present invention is described further with reference to the following example.

I. Experimental Method and Electrolytic Cell

The electrolytic cell is shown in Figure 1.

10

With reference to Figure 1, the electrochemical cell included a graphite crucible equipped with a graphite lid. The crucible was used as the cell anode. A stainless steel rod was used to secure electrical contact between a
15 d/c power supply and the crucible. The cell cathode consisted of Kanthal or platinum wire connected at one end to the power supply and TiO_2 pellets suspended from the other end of the wire. An alumina tube was used as an insulator around the cathode. The cell electrolyte was a
20 commercially available source of CaCl_2 , namely calcium chloride dihydrate, that partially decomposed on heating at the operating temperature of the cell and produced CaO . A thermocouple was immersed in the electrolyte in close
proximity to the pellets.

25

Two types of pellets were used. One type was slip-cast and the other type was pressed. Both types of pellets were made from analytical grade TiO_2 powder. Both types of pellets were sintered in air at 850°C . One
30 pressed and one slip-cast pellet were used in the experiment.

The cell was positioned in a furnace and the experiment was conducted at 950°C . Voltages up to 3V were
35 applied between the crucible wall and the Kanthal or platinum wire. The voltage of 3V is below the potential at which Cl^- anions can deposit on the anode at that

- 9 -

temperature. In addition, the voltage of 3V is above the decomposition potential of CaO and below the decomposition potential of CaCl_2 .

5 The power-supply maintained a constant voltage throughout the experiment. The voltage and resulting cell current were logged using LabVIEW (TM) data acquisition software.

10 At the end of the experiment the cell was removed from the furnace and quenched in water. The solid CaCl_2 was dissolved by water and the two pellets were recovered.

15 II. Experimental Results

 With reference to Figures 2 and 3, the constant voltage (3V) used in the experiment produced an initial current of approximately 1.2A. A continuous drop in the
20 current was observed during the initial 2 hours. After that a gradual increase in the current up to 1A was observed.

 SEM images of the cross-sections of the two
25 recovered pellets are shown in Figures 4 and 5. The SEM images indicate the presence of metallic titanium in both pellets, thereby establishing that the method successfully electrochemically reduced titania.

30 The presence of virtually pure metallic titanium in both pellets was confirmed by EPMA analysis. The analysis also showed areas of partially reduced titania. The EPMA results are shown in Figures 6 and 7.

35 Carbon was detected at various locations within the pellets and its content varied up to 18wt%.

- 10 -

Many modifications may be made to the present invention as described above without departing from the the spirit and scope of the invention.

5 By way of example, whilst the above description of the invention focuses on reduction of titania, the invention is not so limited and extends to reduction of other titanium oxides and to oxides of other metals and alloys. Examples of other potentially important metals
10 are aluminium, silicon, germanium, zirconium, hafnium, magnesium and molybdenum.

 Furthermore, whilst the above description focuses on CaCl_2 -based electrolyte, the invention is not so limited
15 and extends to any other suitable electrolytes (and mixtures of electrolytes). Generally, suitable electrolytes will be salts and oxides that are soluble in salts. One example of a potentially suitable electrolyte is BaCl_2 .

- 11 -

CLAIMS:

1. A method of reducing a metal oxide in a solid state in an electrolytic cell, which electrolytic cell includes an anode, a cathode, a molten electrolyte, the electrolyte includes cations of a metal that is capable of chemically reducing the metal oxide, and the metal oxide in a solid state is immersed in the electrolyte, and which method includes a step of operating the cell at a potential that is above a potential at which cations of the metal that is capable of chemically reducing the metal oxide can deposit as the metal on the cathode, whereby the metal chemically reduces the metal oxide.
2. The method defined in claim 1 includes operating the cell that is above the potential at which cations of the metal that is capable of chemically reducing the metal oxide deposit as the metal on the cathode so that the metal deposits on the cathode.
3. The method defined in claim 2 wherein the metal deposited on the cathode is soluble in the electrolyte and can dissolve in the electrolyte and thereby migrate to the vicinity of the metal oxide.
4. The method defined in any one of the preceding claims wherein the metal oxide is a titanium oxide, the electrolyte is a CaCl_2 -based electrolyte that includes CaO as one of the constituents of the electrolyte, and the cell potential is above a potential at which Ca metal can deposit on the cathode.
5. The method defined in claim 4 wherein the cell potential is below the decomposition potential for CaCl_2 to minimise forming Cl_2 gas at the anode.

- 12 -

6. The method defined in claim 4 or claim 5 wherein the cell potential is less than or equal to 3.5V in a cell operating with the electrolyte at 600-1100°C.

5 7. The method defined in any one of claims 4 to 6 wherein the cell potential is at least 1.3V in a cell operating with the electrolyte at 600-1100°C.

10 8. The method defined in any one of claims 4 to 7 wherein the CaCl_2 -based electrolyte is a commercially available source of CaCl_2 that forms CaO on heating or otherwise includes CaO .

15 9. The method defined in any one of claims 4 to 7 wherein the CaCl_2 -based electrolyte includes CaCl_2 and CaO that are added separately or pre-mixed to form the electrolyte.

20 10. The method defined in any one of the preceding claims wherein the anode is graphite.

25 11. The method defined in any one of the preceding claims wherein the anode is graphite and the electrolytic cell includes a membrane that is permeable to oxygen anions and is impermeable to carbon in ionic and non-ionic forms positioned between the cathode and the anode to thereby prevent migration of carbon to the cathode.

30 12. The method defined in any one of the preceding claims wherein the cathode is formed at least in part from the metal oxide.

35 13. An electrolytic cell reducing a metal oxide in a solid state, which electrolytic cell includes an anode, a cathode, a molten electrolyte, which electrolyte includes cations of a metal that is capable of chemically

- 13 -

reducing the metal oxide, and a metal oxide in a solid
state immersed in the electrolyte, and which electrolytic
cell operates at a potential that is above a potential at
which cations of the metal that is capable of chemically
5 reducing the metal oxide deposit as the metal on the
cathode, whereby the metal chemically reduces the metal
oxide.

14. The cell defined in claim 12 wherein the
10 cathode is formed at least in part from the metal oxide.

1/11

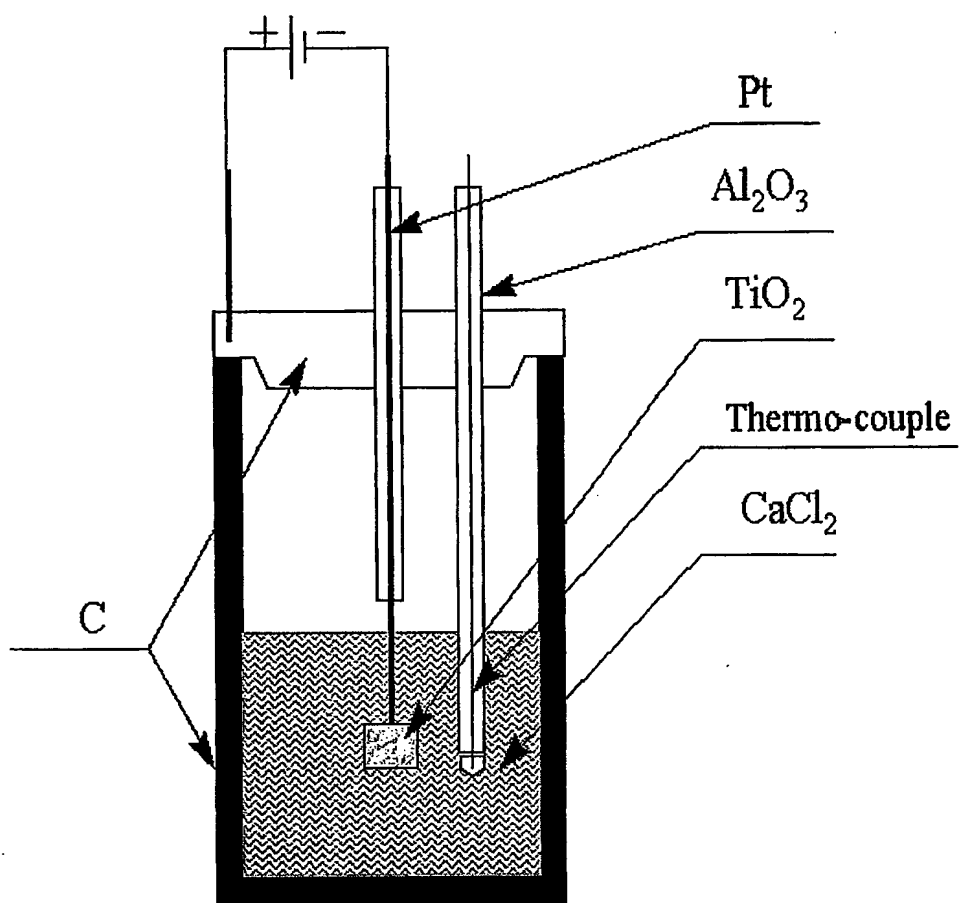


Fig. 1 Schematic of the experimental set up

2/11

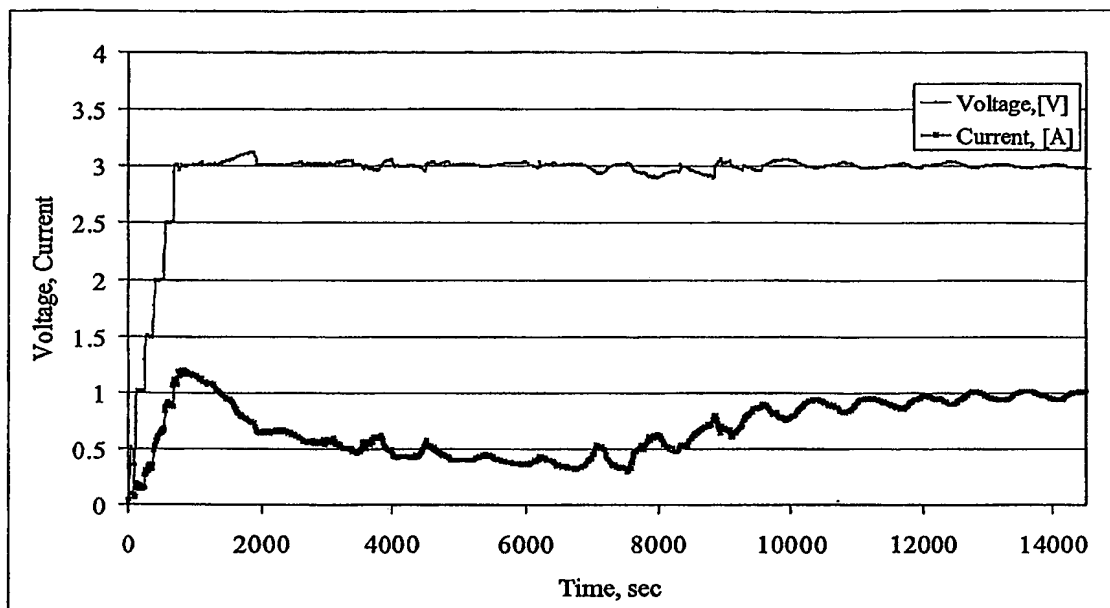


Fig 2. Variation of the applied potential and current during the run

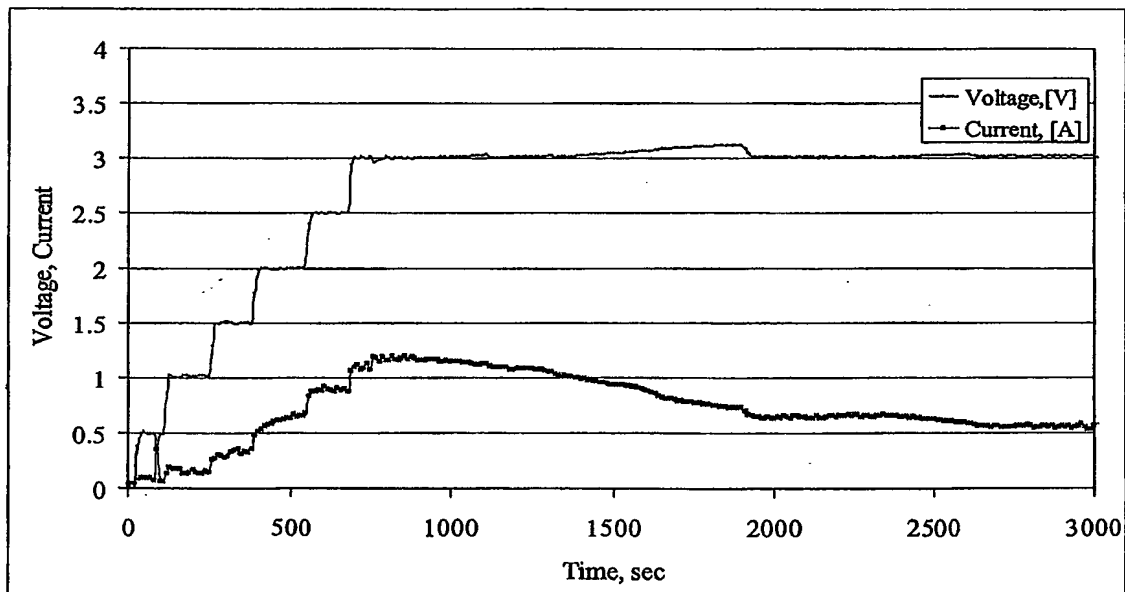


Fig 3. Variation of the applied potential and current in the initial stage of the run

3/11

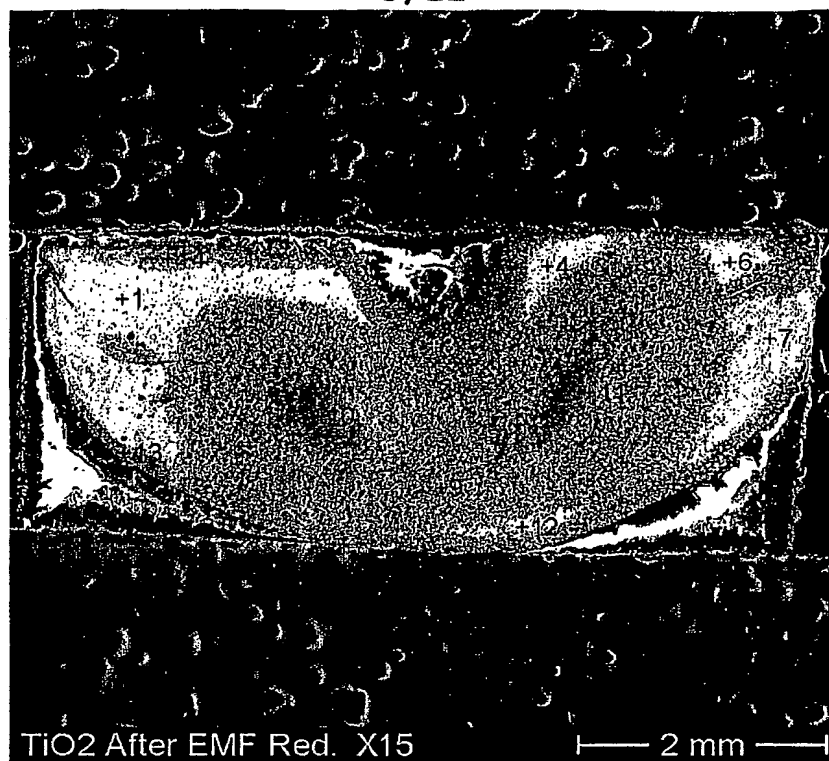


Fig 4. SEM image of the horizontal cross-section of Pellet 1 after the run

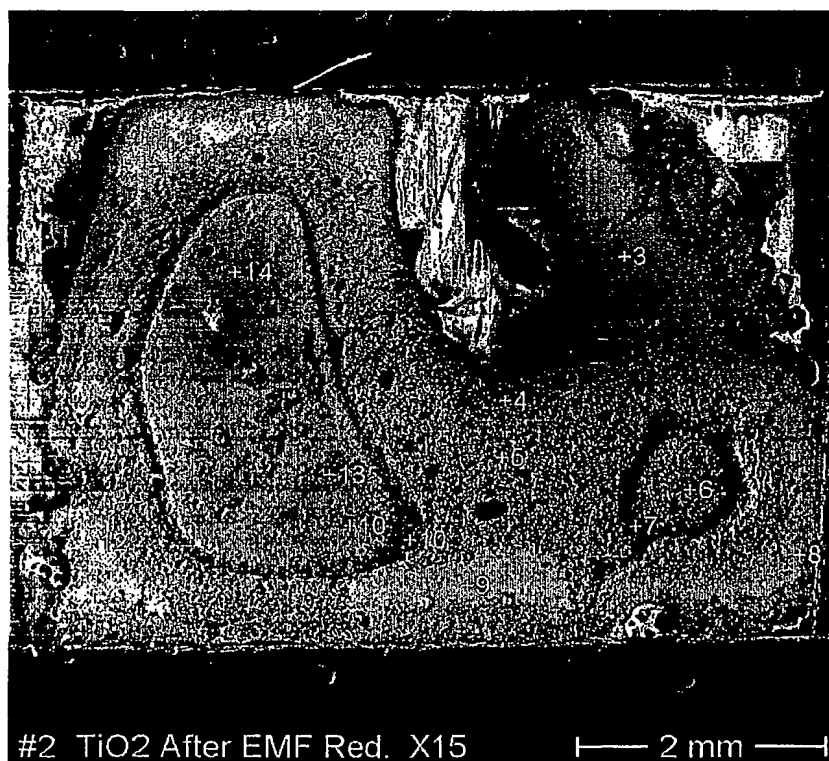
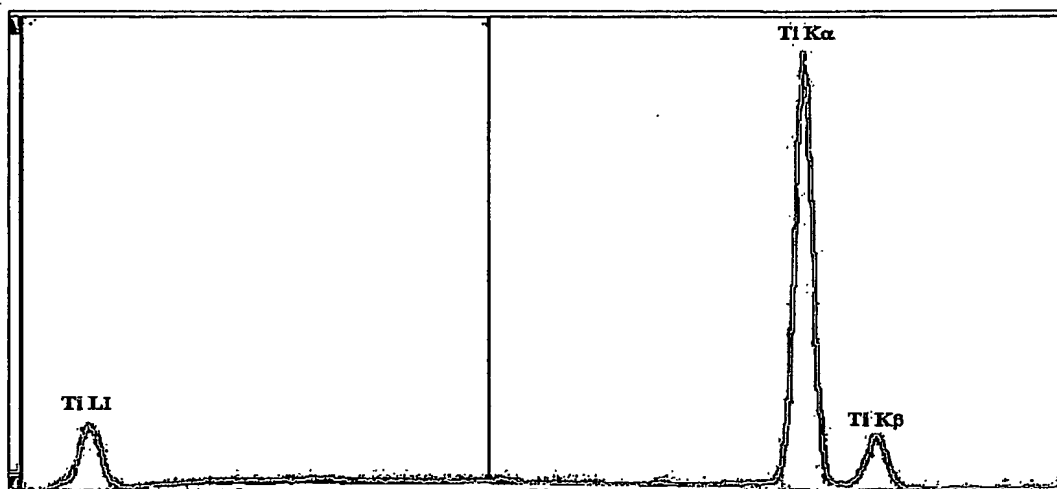
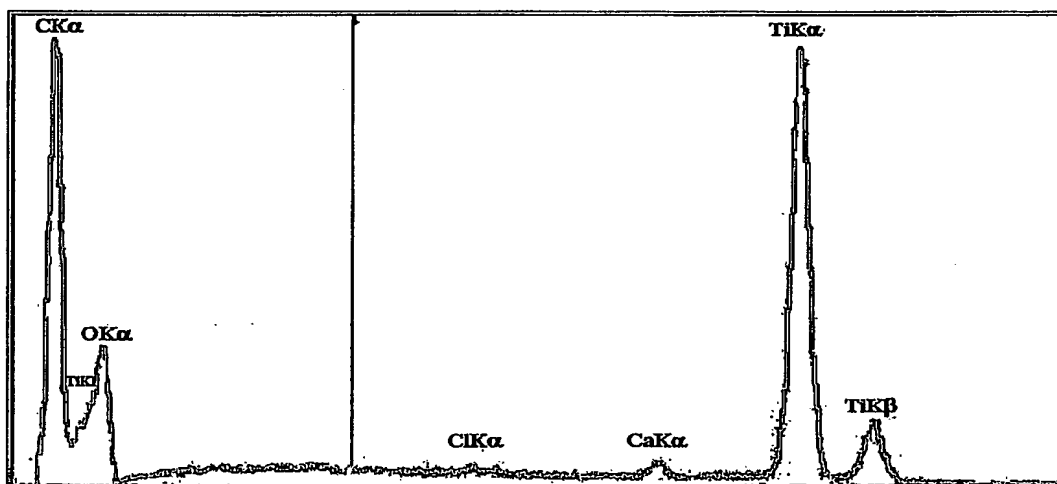


Fig. 5. SEM image of a horizontal cross-section of Pellet 2 after the run

4/11



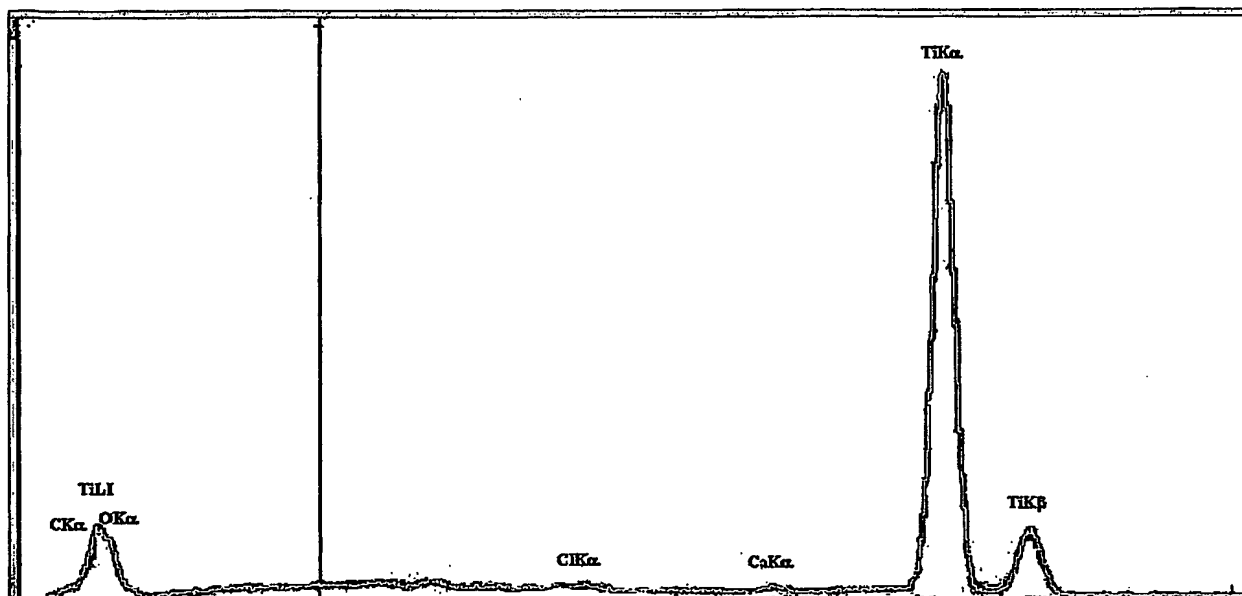
Point 1



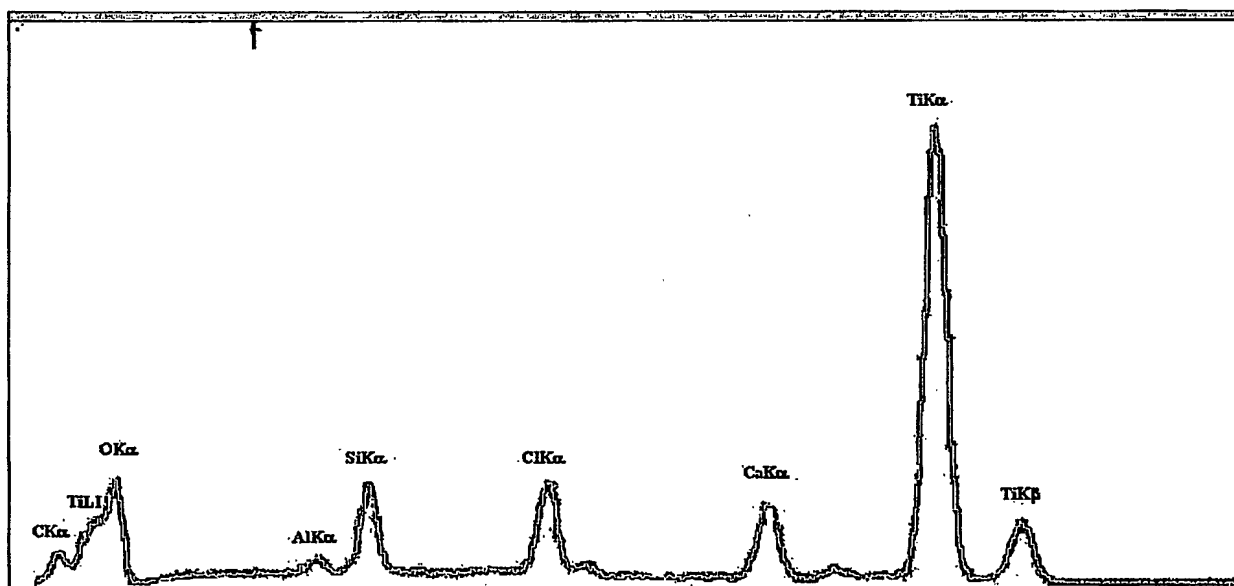
Point 2

Fig. 6. EPMA analysis of Pellet 1 (Pressed)

5/11



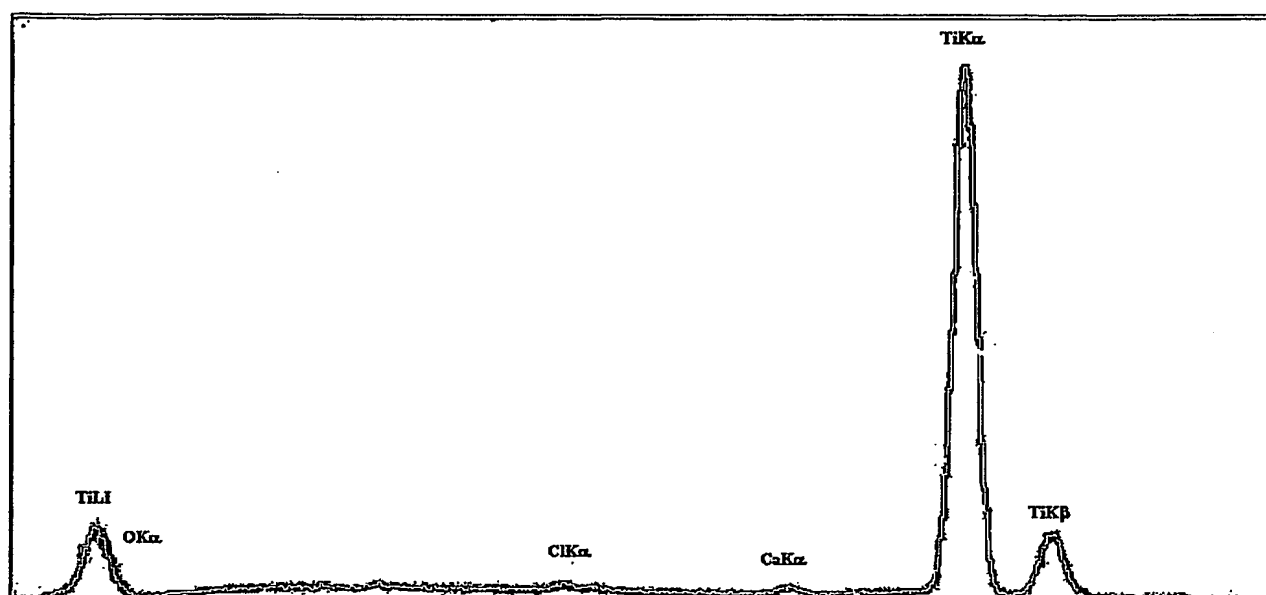
Point 1



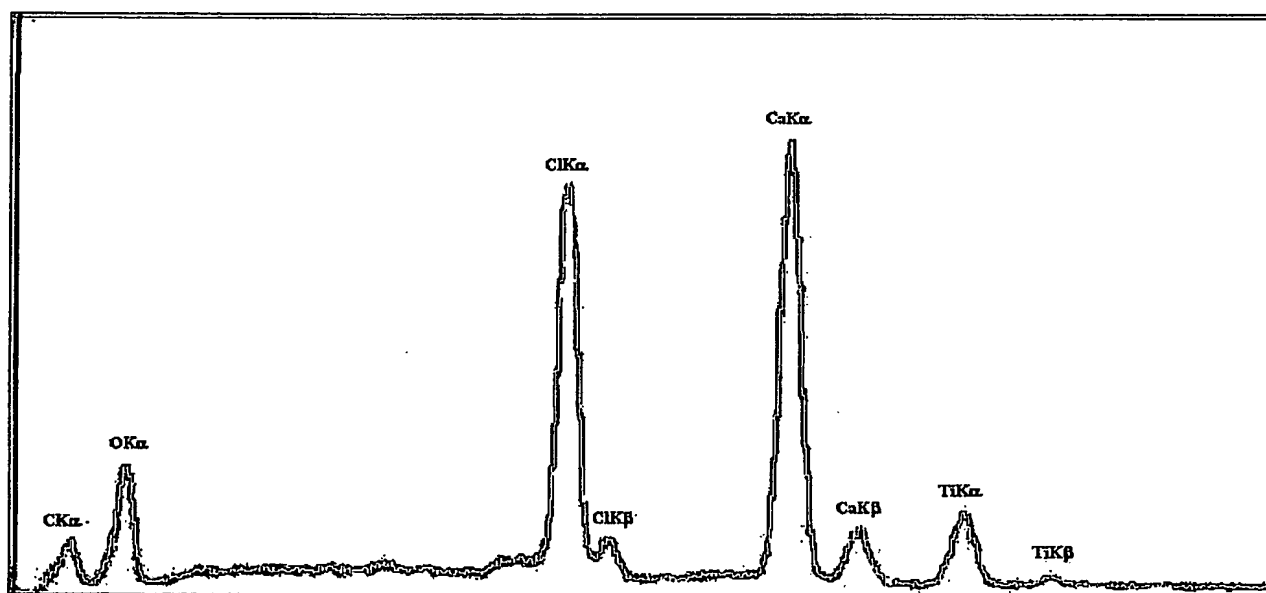
Point 2

Fig. 7. EPMA analysis of Pellet 2 (Slip-cast) - Part 1

6/11



Point 3



Point 4

Fig. 7. EPMA analysis of Pellet 2 (Slip-cast) - Part 2

7/11

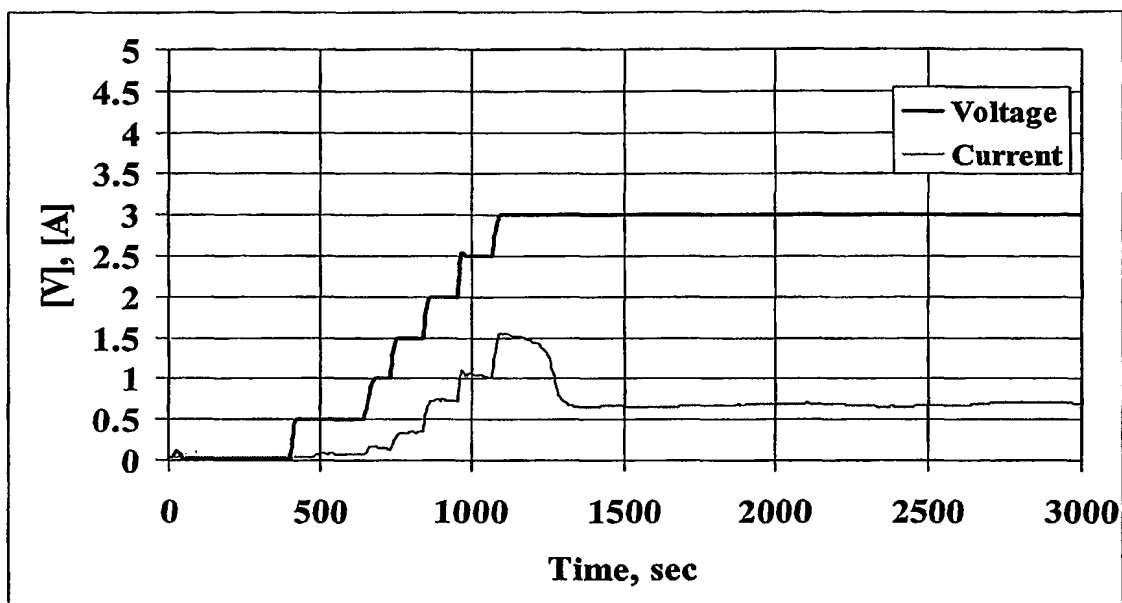


Fig. 8. Variation of the applied potential and current in the initial stage of the run

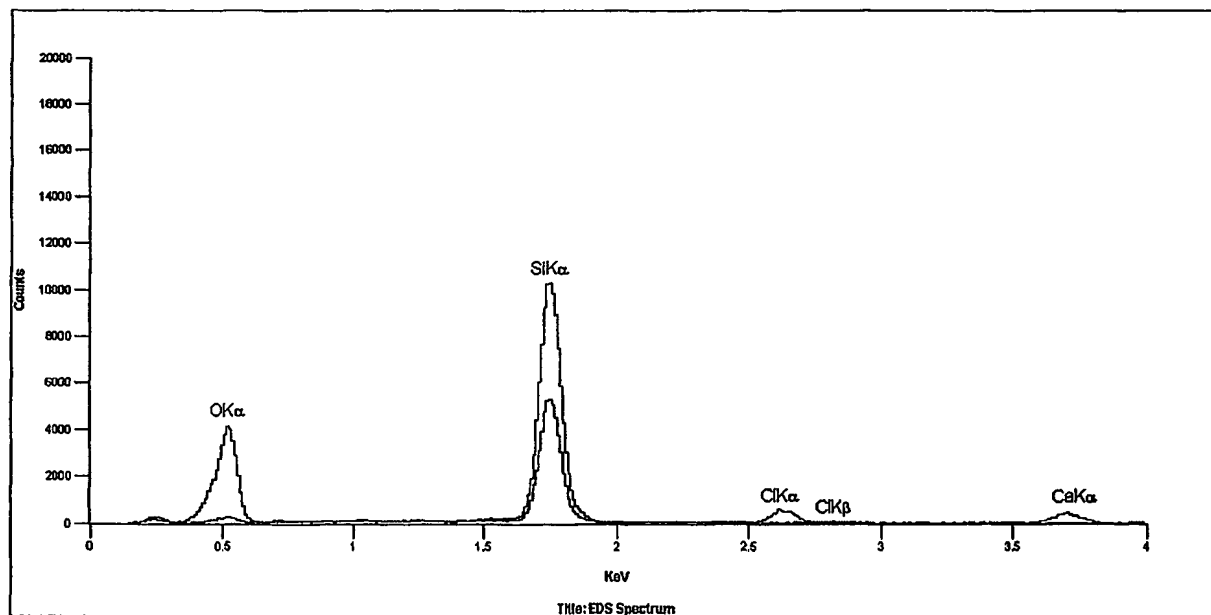


Fig. 9. Comparison of the spectrum of pure SiO_2 with the one of the surface of the sample after reduction

8/11

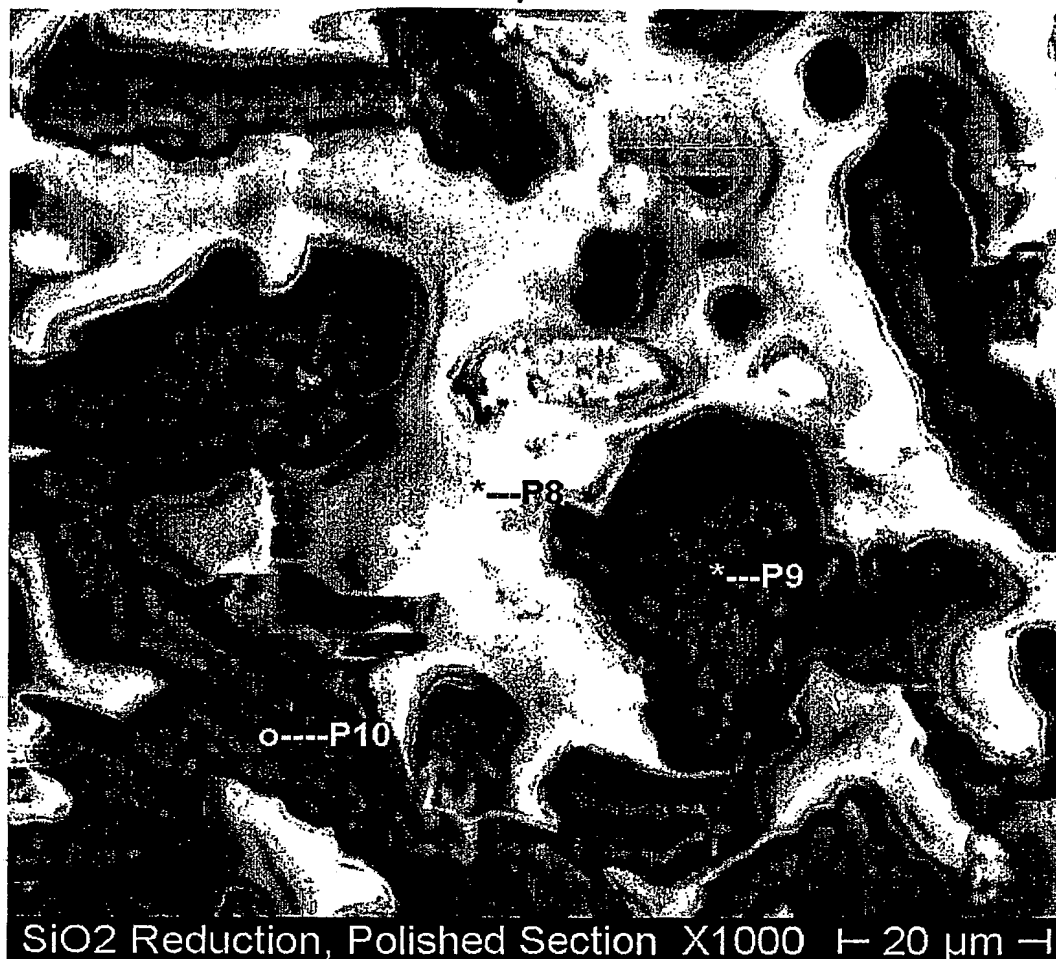


Fig. 10. Appearance of the structure of the SiO₂ pellet after reduction

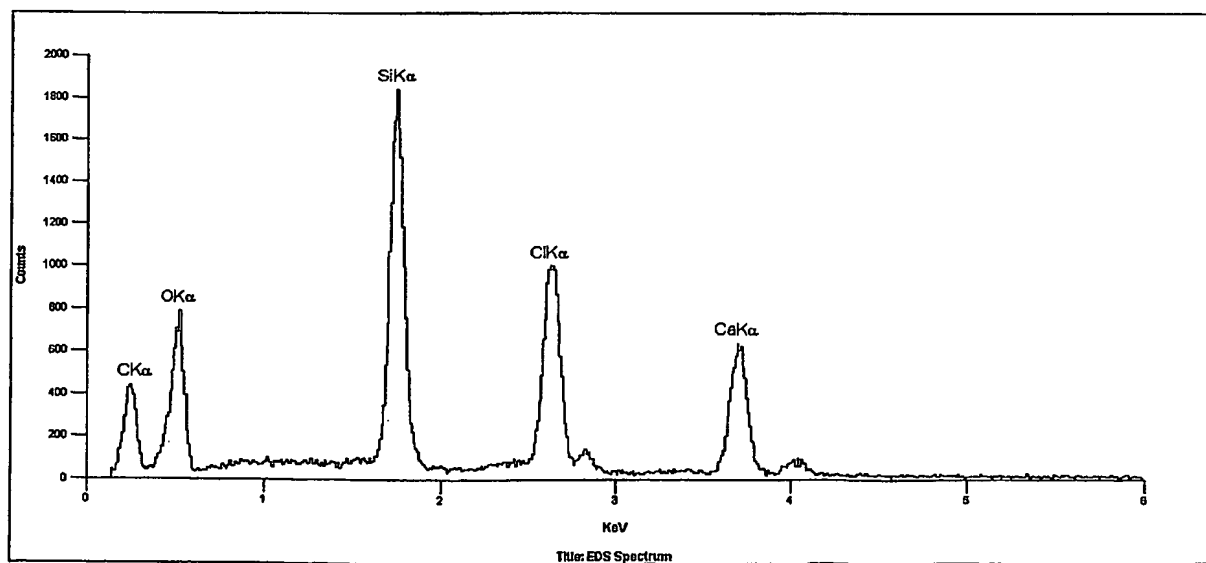


Fig. 11. Spectrum at point 8 in Figure 10.

9/11

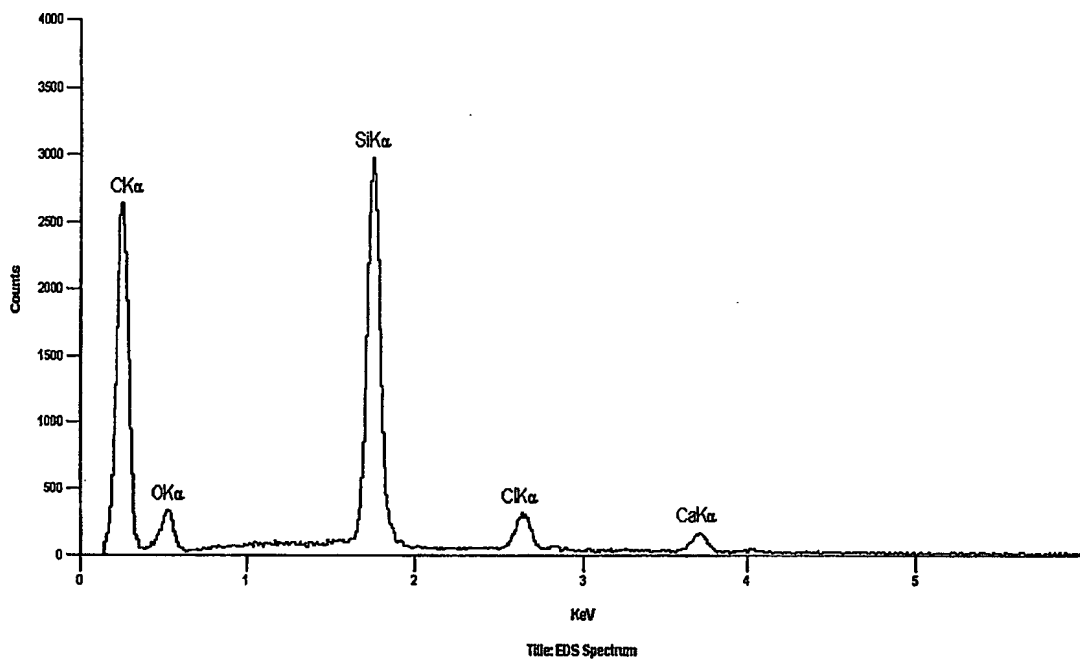


Fig. 12. Spectrum at point 10 in Figure 10.

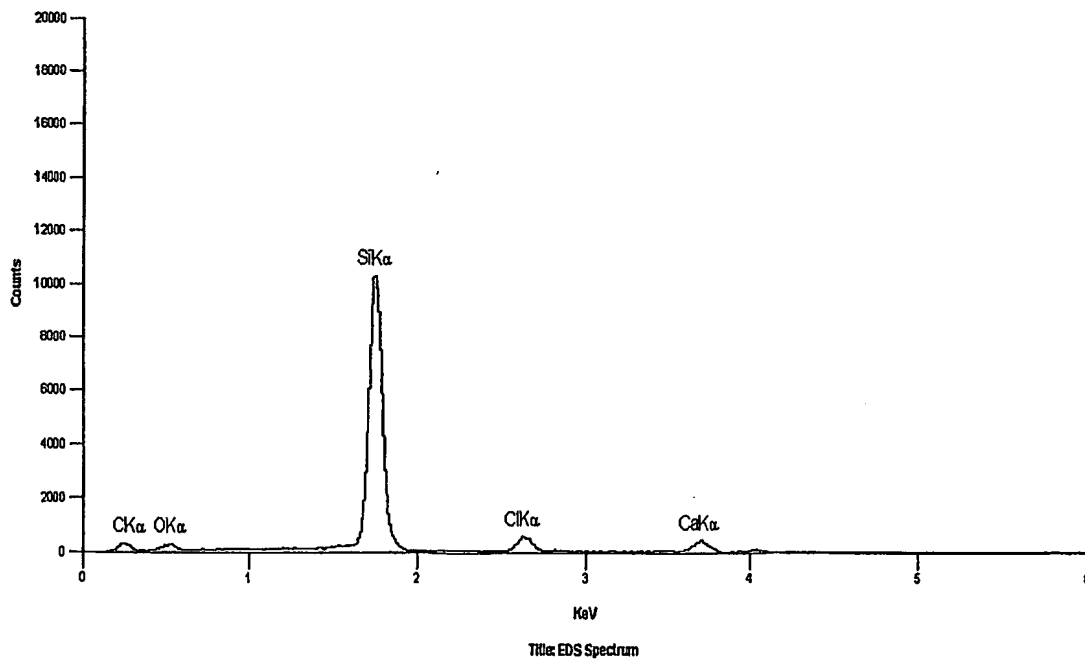


Fig. 13. Spectrum at point 10 in Figure 10.

10/11

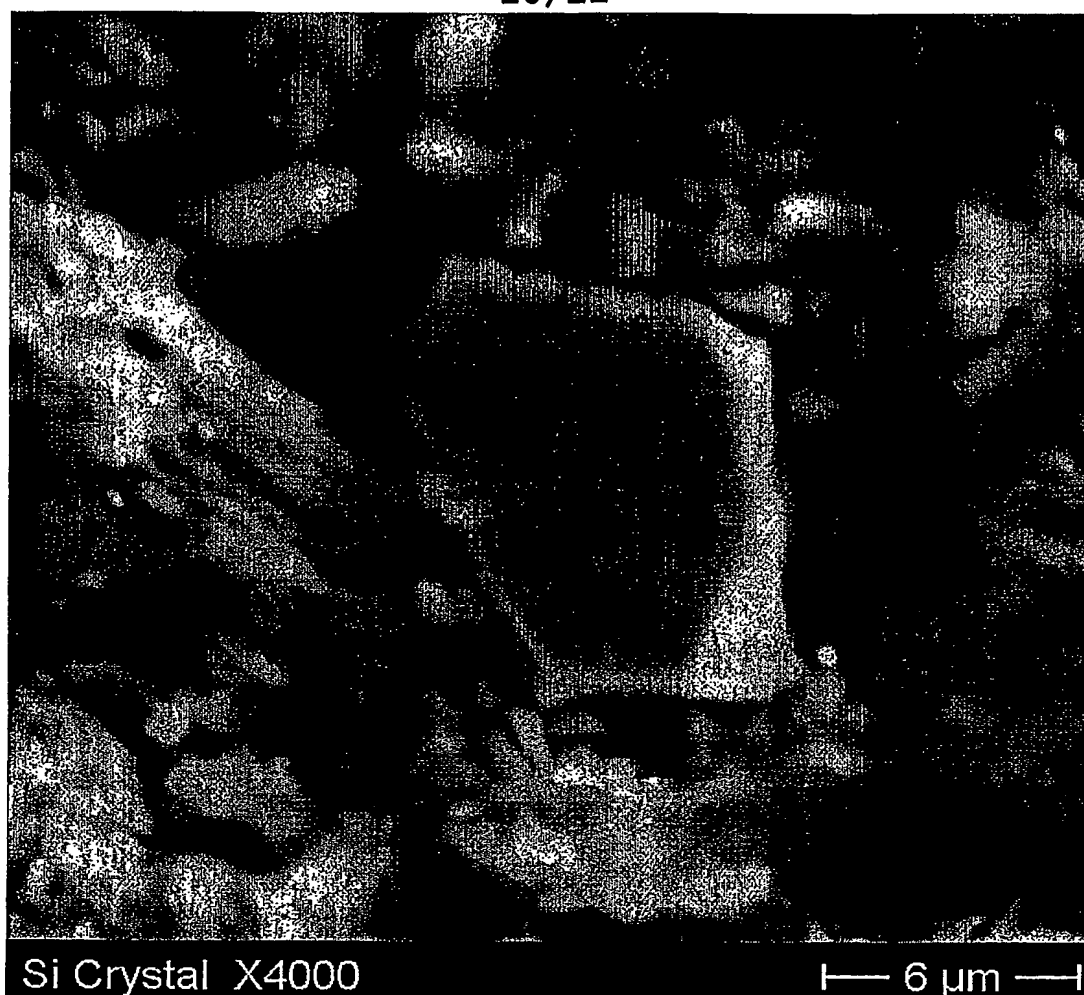


Fig. 14. Silicon crystal found in the pellet after reduction

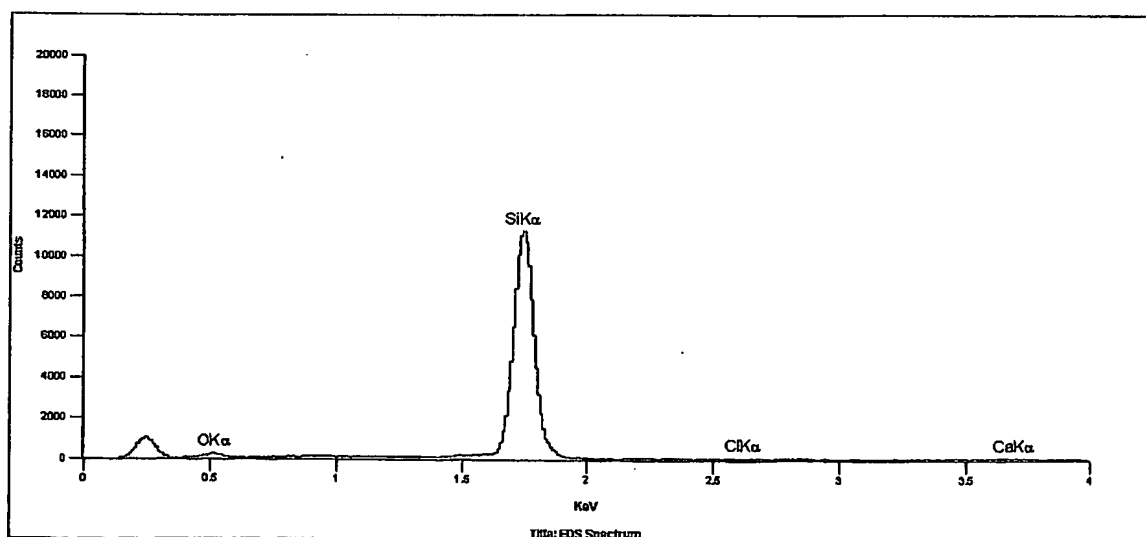


Fig. 15. Spectrum of the crystal in Figure 14.

11/11

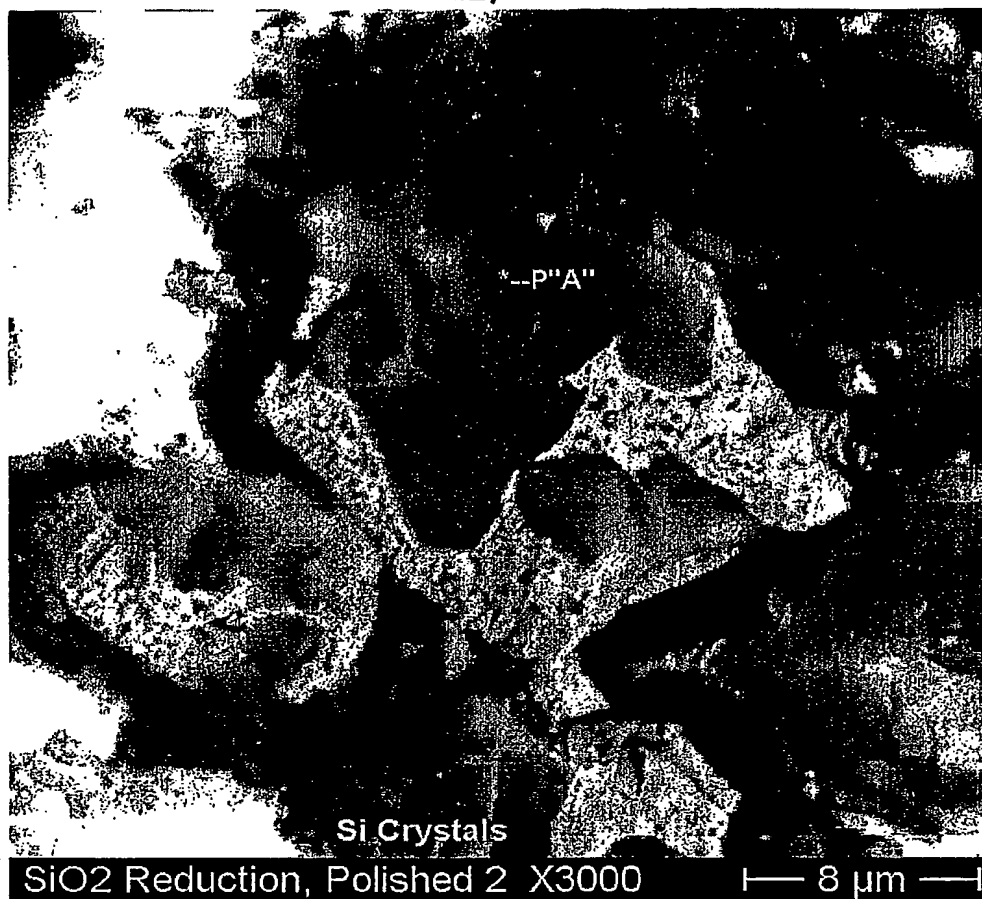


Fig. 16. Silicon crystal found in the pellet after reduction

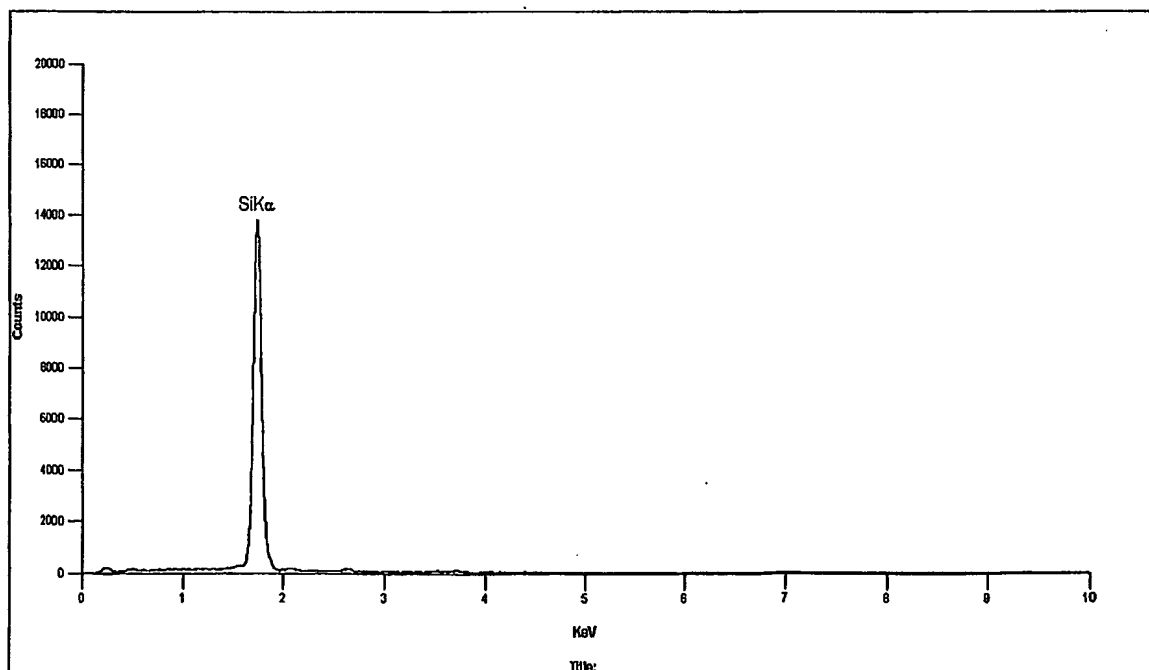


Fig. 17. Spectrum at point A in Figure 16.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU03/00306

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : C25C 3/28		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DWPI: C25C 5/04, C22B 34/12, and KEYWORDS: reduc+, electro+ E-space: C25C 3/00		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 03/002785 A (BHP BILLITON INNOVATION PTY LTD) 9 January 2003 Whole document, especially claims 1-9	1-14
P,X	WO 03/016594 A (BHP BILLITON INNOVATION PTY LTD) 27 February 2003 Pages 5, 9-12, and claims	1-14
P,X	WO 02/083993 A (BHP BILLITON INNOVATION PTY LTD) 24 October 2002 Whole document	1-14
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
<p>* Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"B" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>		
Date of the actual completion of the international search 16 April 2003		Date of mailing of the international search report 30 APR 2003
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929		Authorized officer THARU FERNANDO Telephone No : (02) 6283 2486

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU03/00306

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2359564 A (THE SECRETARY OF STATE FOR DEFENCE) 29 August 2001 Whole document	1-14
A	WO 99/64638 A (CAMBRIDGE UNIVERSITY TECHNICAL SERVICES LIMITED) 16 December 1999 Whole document	1-14
A	US 6074545 A (GINATTA) 13 June 2000 Whole document	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/AU03/00306

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
WO	03002785	NONE					
WO	03016594	NONE					
WO	02083993	NONE					
WO	9964638	AU	42770/99	BR	9910939	CA	2334237
		CZ	20004476	EP	1088113	HU	200102934
		NO	20006154	PL	344678		
GB	2359564	AU	200133871	AU	200133876	AU	200133890
		EP	1257677	EP	1257678	EP	1257679
		GB	2376241	US	2003057101	WO	200162994
		WO	200162995	WO	200162996	GB	2362164
US	6074545	AU	81918/98	BR	9807156	EP	958409
		IT	TO		970080	NO	993455
		NZ	337553	WO	9833956	ZA	9800897
END OF ANNEX							

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: Dark

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.